A New Method for Coating Highly-Permeable Matrices for High-Power ISOL Production Targets

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Abstract

A relatively simple and inexpensive infiltration coating technique has been developed for depositing refractory target materials onto highly-permeable matrices to form short diffusion-length production targets for ISOL applications. The method is based on a suspension of finely divided (ϕ: ~1 μm) target materials (e.g. carbides, oxides, sulfides, etc.) in a binder to form a paint that can be vacuum infiltrated to uniformly coat the surfaces of highly-permeable, fibrous matrices such as reticulated-vitreous-carbon-fiber (RVCF). The coating operation is followed by thermal treatment under high vacuum conditions to evaporate the binder and, if possible, to sinter the material. The technique has been used to coat RVCF matrices with a number of refractory metal-carbides and metal-oxides for potential use as high power, short diffusion-length spallation and fission production targets at the RIA. Initial on-line tests of a CeS target that was manufactured using this process have been completed. An on-line release measurement of ^{34}Cl from this CeS target resulted in beam intensities of about 10^4 ions per second and the presence of molecular ions (aluminum chloride) was also confirmed. Inspection of the target material after irradiation showed no damage, indicating that this method can be used to make viable ISOL production targets.

ISOL Production Targets

Target issues present a challenge for present and next-generation ISOL based facilities such as RIA. Beams of short-lived radioactive species produced by the ISOL method are often difficult to generate with high intensities, since the species of interest must be diffused from the target, effusively transported to an ion source, ionized, extracted, mass analyzed, and accelerated to research energies in a time commensurate with their lifetime. Time delays associated with these processes result in decay losses and can significantly reduce the beam intensities of short-lived radioactive species. To minimize such decay losses, target materials must exist as micron-scale fibers or be uniformly deposited in thin layers onto mechanically and thermally stable highly-permeable matrices that can operate at elevated temperatures. Although a number of methods for depositing thin layers of target material onto surfaces are available, the methods are generally expensive, slow, and either inappropriate for coating interior surfaces of highly-permeable complex matrices (non-infiltrating, non-penetrating) or require complex chemical processes that are only available for depositing specific elemental or compound materials.

The objective of this research effort is to develop an inexpensive and universal method for coating complex-geometry matrices with refractory compounds or metals to

prescribed thicknesses for use as ISOL production targets at RIA. Several target-coating schemes have been used or are under consideration for this purpose; they include: chemical vapor deposition/chemical vapor infiltration (CVD/CVI); chemical reaction deposition (CRD); physical vapor deposition (PVD); sputter deposition (SD); electroplating deposition (EPD), electrophoresis deposition (ED), sol-gel coating (SGC) and atomic layer deposition (ALD). However, most production target designs require deposition of controlled thickness of refractory compound materials onto the interior surfaces of highly permeability (low density) matrices for which some of these techniques are not appropriate. For example the PVD and SD techniques are limited to line-of-sight deposition while the penetrating techniques of CVD/CVI, sol-gel, and ALD require a sequence of complex chemical reactions for which schemes for deposition of a restricted number of compounds have been developed. Chronically lacking from the list of penetrating methods is a universal method that is fast and inexpensive that can be directly used to deposit controlled thicknesses of refractory compound materials onto complex structure matrices.

'Paint' Coating Technique

A new coating technique has been developed that holds promise as a close-to-universal method for uniform deposition of thin layers of target materials onto highly permeable matrices to form production targets. The methodology is based on the vacuum coating of a binder-suspended, finely divided target material (ϕ: ~1 μm) onto a highly-permeable, rugged support matrix. In cases where the target material and the matrix may interact, the matrix can be pre-coated with a thin inert layer to prevent reduction reactions.

The requirement of high permeability connotes low-density, open-structure target matrices with large surface areas for the controlled deposition of thin layers of the production target material. Reticulated vitreous carbon fibers (RVCF) [1] and carbon-bonded-carbon fibers (CBCF) [2] offer highly-permeable, machinable matrices for deposition of generic target materials onto their surfaces. CBCF has a density that is 10% of nominal graphite density and is made of cylindrical fibers with ~6μm diameter. The fibers are sintered together at the points of intersection in a random distribution. RVCF is a tetrakai-decahedral continuous ligament structure (see Figure 1) that can be compressed in orthogonal directions during the curing process. This feature gives a wide range of target densities with the same thickness of the deposited layer due to the various surface-to-volume ratios that are available. The structure is interesting in that the ligaments have equilateral triangular cross-sections with edge widths of ~75 μm and lengths of ~253 μm. Each cell has 36 legs with each leg shared by three adjacent cells. Thus,

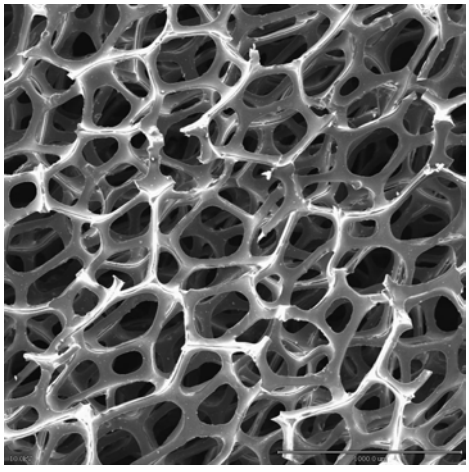

Figure 1. A scanning electron micrograph of an uncoated RVCF matrix.

the effective number of legs per cell is 12. Assuming the unit cell is spherical, the average diameter of each cell is ~758 μm. Since we need to uniformly coat the surface of the fibers with the chosen target material, the surface area per unit volume is of primary interest. The available RVCF surface-to-volume ratios are 25.6 cm^2/cm^3, 51.21 cm^2/cm^3, 102.44 cm^2/cm^3, and 204.84 cm^2/cm^3, depending on the compression.

The target material of interest must be refractory to be useful at high temperatures and it must be in a form that can be suspended in a binder, specifically, it must be a finely-divided powder. The target material of interest is reduced to sub-micron particles with an ultra-sonic milling device. A laboratory scale, high-energy shaker mill [3] was used to rapidly pulverize powder samples while mixing them homogeneously. The device mills samples by placing them in a container along with one or more milling media, and imparting motion to the container. The containers are usually cylindrical; the milling media are most often balls but may be rods, cylinders, or other shapes. Generally the containers and milling media are made from the same material. As the container is rolled, swung, vibrated, or shaken, the inertia of the milling media causes them to move independently, into each other and against the container wall, milling the sample. Examples of ZrC and HfC powders thus produced are shown in Figure 2.

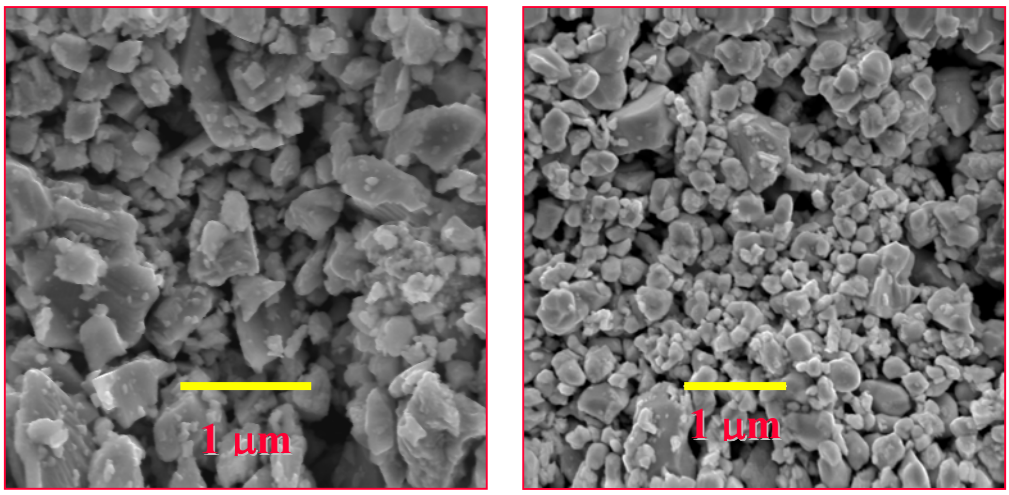

Figure 2. Scanning electron micrographs of finely-divided powders after milling, ZrC on the left and HfC on the right.

The paint binder is commercially available [4] and consists of a weight mixture of about 50% ethanol, 49% ethyl aceto-acetate, and 1% gum cellulose. The finely divided target material powder is mixed with this binder in an initial volume of 5% target material to 95% binder to form a paint. The solution is then diluted by adding additional binder to achieve the desired mass of target material per unit volume. The thickness of the layer of target material that is deposited onto the fibers of the matrix depends on the weight gain of a sample, which depends on the concentration of target material in the paint.

The coating apparatus is very simple and is shown in Figure 3. It consists of a 100 mm diameter × 50 mm tall cylindrical Pyrex beaker with an "O"-ring sealed Teflon-cover pressed into the top of the beaker. A tapered (45 degree) cavity is machined into the top

face of the cover for capturing individual 15.25 mm × 2 mm thick RVCF disks. A 1-mm diameter hole is drilled from the apex of the taper through the Teflon cover plate for pulling air through the sample during infiltration coating of a particular target when connected to a mechanical vacuum pump. A vacuum fitting is attached to the Teflon cover plate for evacuating the beaker to slightly negative pressures through a small needle valve. A small beaker is positioned immediately under the target for capturing excess target material/binder fluid that does not adhere to the RVCF target matrix during the infiltration coating process.

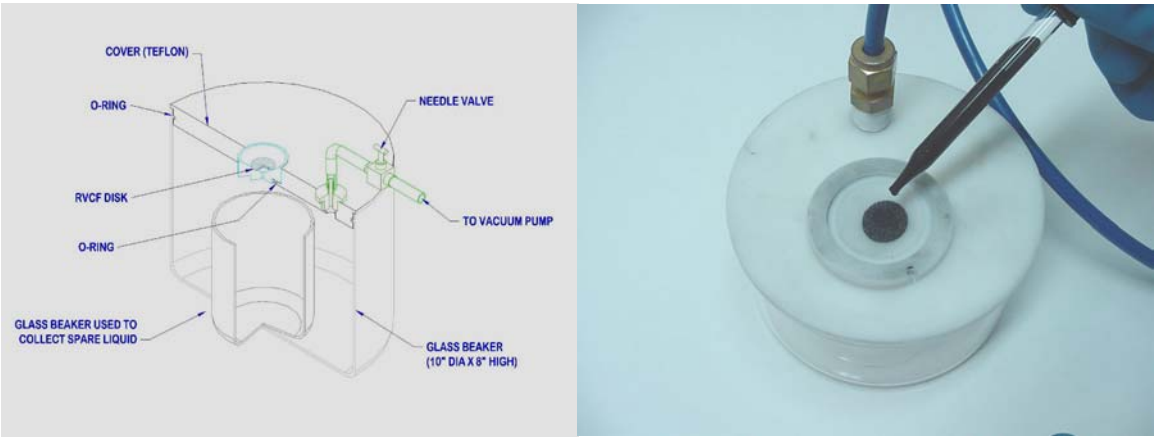

Figure 3. A drawing and a photograph of the vacuum infiltration apparatus used for making targets using the paint coating technique.

Each target matrix is placed in the tapered holder and the needle valve is opened to the vacuum side of the small mechanical vacuum so that air flows through the target matrix. The rate of pumping is carefully controlled by adjusting the needle valve so as to ensure slow transfer of the solution to the RVCF sample while avoiding breakage of the target matrix. Each target RVCF disk is carefully weighed before coating. The following procedures are used for coating a particular sample: 1) after establishing a slight negative pressure on the system, the target material/binder solution is aggressively shook to ensure uniform density within the mix; 2) an eye-dropper is then used to withdraw target material/binder solution from the container and to uniformly aspirate the target material/binder solution over the sample surface; 3) after the fluid has been pulled through the sample, it is turned over using tweezers in an effort to ensure uniformity in coating; 4) following the coating operation, each sample is carefully examined for visual uniformity; 5) all samples that pass the visual examination are allowed to air-dry for at least 24 hours; 6) each sample is then carefully weighed to establish the weight gain of target material plus binder before heating.

Following coating, samples are out-gassed in a vacuum furnace that is evacuated to a pressure of ~100 mbar and purged a few times with argon to displace trace amounts of ambient N_2 and O_2. The temperature of the targets is gradually increased linearly over a three-hour period to a temperature of 1123 K. After reaching 1123 K, the samples are held at this temperature for one hour before gradually cooling down to ambient temperature over the same 3 hour time period to avoid thermal stresses that could lead to

flaking of the target material. This operation is designed to decompose and drive off volatile components of the residual cellulose binder (decomposition temperature: 623 K). Following cool down, each sample is carefully reweighed to establish the true weight gain of the coating operation and to establish a relation between the weight gain for *fired* and *unfired* targets. Following heat treatment, the targets are visually inspected for material adherence to the substrate and tendencies to flake. The samples are then stored in an inert atmosphere (*Ar*) to prevent moisture pick-up prior to evaluation.

Using this paint coating technique, sample targets have been manufactured from eleven different target materials. Materials used thus far are; BN, SiC, TiC, NbC, VC, ZrC, HfC, Al_2O_3, ZrO_2, Y_2O_3, and CeS. Samples of these targets are shown below in Figure 4. All of the materials listed above have been deposited onto RVCF matrices but in some cases the matrix was pre-coated with a thin layer of tungsten to prevent reactions between the target material and the carbon substrate. At this time, only one of these targets (CeS) has been tested on-line, but many more will be tested in the coming months.

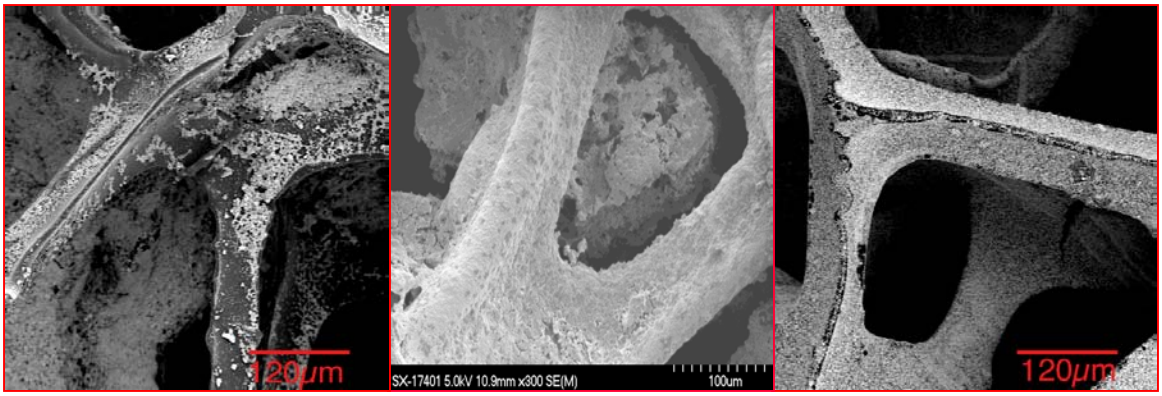

Figure 4. Scanning electron micrographs of various targets made using the paint coating technique (ZrC on the left, CeS in the middle, and Al_2O_3 on the right).

On-line Measurements using a CeS Target

Once the targets have been made, a series of tests must be made to determine if they will be useful as ISOL production targets. The target samples are first put into a target holder that is coupled to an ion source and heated to the maximum operating temperature for the given material to determine if any volatile components are still present in the sample, which could affect the operation of the ion source. The samples are visually inspected after heating to determine if there has been any physical change that would limit the operational lifetime of the targets. If these tests are satisfactory, an on-line production and release measurement is made to determine if the isotopes of interest will be released.

Initial tests of a CeS target are encouraging. The CeS layer (5 µm) is deposited onto a RVCF matrix that was pre-coated with a thin layer (~2µm) of tungsten. No volatile components were observed when the target was heated to 2273 K and the target disks appeared to be unchanged after a period of four days at this elevated temperature. Using a 40 MeV, 25 nA deuteron production beam, ^{34}Cl was produced in the target using the

$^{34}S(d,2n)^{34}Cl$ reaction. This target was coupled to a positive-ion plasma-type ion source and a beam of ^{34}Cl was extracted with a beam intensity of about 10^4 ions per second in the mass-34 beam and a similar yield in a molecular sideband, aluminum chloride. Very little aluminum vapor was present in the target during the initial tests, so further tests will focus on trying to increase the yield of chlorine by adding sufficient aluminum vapor to saturate this channel and to see if there are any adverse affects on the target material.

Status and Future Plans

Development of this technique was a major portion of the PhD thesis work of one of the authors (JCB) and while the thesis has been completed, work is continuing in attempt to discover the full potential of this coating technique and to produce many more useful ISOL production targets. Using this paint-coating technique, we have manufactured targets from eleven different refractory compounds and have demonstrated that the technique has the potential to be widely applicable. One of these targets, CeS/RVCF, has been tested on-line and the release measurements have shown that radioactive chlorine atoms will release from the target material. Additional measurements are needed to determine the release rate and what coating thickness is optimal for short-lived isotopes.

More testing of each of the targets mentioned above is needed to determine the capability of these target matrices to withstand high temperatures and whether the isotopes of interest will release from the target matrix at a rate that is fast enough to be useful (i.e. release rates that are relatively fast when compared with the radioactive half-life). Uranium carbide targets will soon be manufactured using this technique and the yields of fission fragments will be measured and compared to those measured from other UC targets that are prepared using a 'wet chemistry' deposition technique [5]. In addition, the useful production lifetime of these UC targets at high temperatures is important and this will be measured on-line using production beams available at the HRIBF.

The open questions with respect to targets produced using this technique are; will the target material 'stick' to the fibers of the support matrix at high temperatures, what is the operational lifetime, and are the achievable coating thicknesses appropriate for the production and release of the element of interest. These questions will be answered for many of the different target materials in future on-line tests.

References

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